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(71)Applicant : FUJITSU LTD
(72)Inventor : YOSHIDA KENSUKE
YOSHIDA HIROAKI

(54) MANUFACTURING METHOD FOR SOLID ELECTROLYTE, SOLID ELECTROLYTE, AND LITHIUM BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for manufacturing solid electrolyte with lithium ion conductivity at a low temperature in a short time, to provide the solid electrolyte manufactured thereby, and to provide a lithium battery provided with the solid electrolyte.
SOLUTION: This manufacturing method for the solid electrolyte containing lithium, titanium, phosphorus, and oxygen and having the lithium ion conductivity heats precursor solution including nonhydrolyzable organic titanium compounds as a titanium supply source and incinerates it without any gelation process.

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CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of a solid electrolyte which heats the precursor solution which is the manufacture approach of a solid electrolyte of having lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, and contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply, and is characterized by calcinating without passing through a gelation process.
[Claim 2] Said organic titanium compound is the manufacture approach of a solid electrolyte according to claim 1 which is dihydroxy titanium screw lactate or a dihydroxy titanium screw lactate derivative.
[Claim 3] Said precursor solution is the manufacture approach containing a phosphoric acid or a phosphoric-acid metal salt of a solid electrolyte according to claim 1 or 2 as the Lynn source of supply and an oxygen supply.
[Claim 4] The solid electrolyte which is a solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, forms the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to a base material, heats the coat concerned, and is characterized by being formed by calcinating without passing through a gelation process.
[Claim 5] It is the lithium cell characterized by having been a lithium cell equipped with the solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, for said solid electrolyte having formed the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to the positive-electrode object and/or the negative-electrode object, having heated the coat concerned, and forming it by calcinating without passing through a gelation process.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of a solid electrolyte of having lithium ion conductivity, the solid electrolyte manufactured by this, and a lithium cell.
[0002]
[Description of the Prior Art] Since it has the features of it being lightweight and having a high energy consistency, a lithium cell is used in many cases as the memory maintenance power sources in pocket electronic equipment and drive power sources, such as a cellular phone and a notebook computer. A lithium cell is equipped with the electrolyte which generally permits migration of a lithium ion between the positive electrode which comes to include a lithium ion the positive active material in which charge and discharge are possible, the negative electrode which comes to contain negative-electrode active materials, such as an ingredient in which a dope and a dedope of a lithium are possible, and a lithium alloy, and a positive electrode and a negative electrode, and is constituted as a rechargeable battery.
[0003] To the lithium secondary battery, the demand of thin-shape-izing and the further formation of a high energy consistency is increasing with the formation of small lightweight of a portable information device etc. in recent years. Although the nonaqueous electolyte of lithium ion conductivity was generally conventionally used as an electrolyte of a lithium secondary battery, in recent years, the solid electrolyte attracts attention that it should correspond to the demand of thin-shape-izing of a lithium secondary battery, and the formation of a high energy consistency.
[0004] As a solid electrolyte, the gel electrolyte, the intrinsic polymer electrolyte, and the inorganic solid electrolyte are known. In the lithium cell, since it cannot need reinforcing materials, can function also as an inter-electrode separator, and does not produce a liquid spill, even if it thin-film-izes it, since an inorganic solid electrolyte is high intensity and it has the advantage that safety is high, it attracts attention especially as a solid electrolyte of a lithium cell application.
[0005] As an inorganic solid electrolyte in which lithium ion conductivity is shown, the glass of a Li3N single crystal and LiI-Li2 S-P2S5 system, LiI-Li2S2-B-2S3 system, and LiI-Li2 S-SiS4 system is known conventionally. However, since these ingredients are chemical and thermally unstable, they are not practical as an electrolyte of a lithium cell.
[0006] Then, research of the oxide solid electrolyte of a crystallized glass system is active in recent years as an inorganic solid electrolyte in which lithium ion conductivity is shown. As a typical thing, the thing of a LISICON mold expressed with the proximate composition type LiM (PO4) 3 (M=Ti, Zr, germanium, Hf) is mentioned. Generally in the oxide solid electrolyte of a LISICON mold, improvement in lithium ion conductivity is achieved by carrying out the element permutation of a part of M. For example, in Li1+XAlXTi2-X (PO4)3 by which Ti is chosen as M in the proximate composition type of upper **, and a part of Ti concerned is permuted with aluminum, it is possible to attain high ion conductivity called 7x10-4 S/cm at a room temperature. Such a crystallized glass system oxide solid electrolyte is comparatively stable chemically and thermally, and useful as a solid electrolyte of a lithium cell. The lithium secondary

battery equipped with the oxide solid electrolyte of such a LISICON mold is indicated by JP,2002-42876,A.

[0007]

[Problem(s) to be Solved by the Invention] In manufacture of inorganic solid electrolytes, such as an oxide solid electrolyte, scorification or a sol-gel method is adopted conventionally. Scorification is the technique of cooling this and forming the predetermined crystal structure, after forming the network of a configuration element according to solid phase reaction. Therefore, in order to intercrystallize a raw material, very a lot of heat is needed. Moreover, since advance of solid phase reaction is slow, the conclusion of a reaction takes long duration. In manufacture of a LISICON mold solid electrolyte, the raw material mixture which consists of each powdery element source of supply is heated and fused to an about 1500-degree C elevated temperature for example first. After maintaining a melting condition for 1 to 2 hours, whenever [stoving temperature] is lowered, and it considers as the condition of the solid solution thru/or a solid-state, and heats at about 800 degrees C for 12 hours or more. Then, a temperature up is carried out again and it heats above 1000 degrees C for 24 hours, and this is cooled and the target solid electrolyte is obtained. Thus, in order to obtain a solid electrolyte with scorification, great heat and time amount are needed. In addition, it is difficult to compound a solid electrolyte massive according to scorification, and to form the solid electrolyte thin film of the thickness of micrometer order from the massive object concerned.

[0008] On the other hand, a sol-gel method is the technique of burning and hardening this and forming the predetermined crystal structure, after forming the network of a configuration element by the hydrolysis reaction in a solution system. Therefore, an elevated-temperature process like scorification is not needed. However, in order to form a suitable network, by advancing hydrolysis slowly on quiet conditions, it must gel through a sol condition about a raw material solution, and a long time is required rather than scorification. In manufacture of a LISICON mold solid electrolyte, the alcoholic solution containing each element source of supply is first solated at 25-80 degrees C, for example. Next, the sol concerned is left one day to about one week, and is made to gel at 25-120 degrees C. Then, heating baking of about 1 hour is performed at 800-900 degrees C, this is cooled and the target solid electrolyte is obtained. Thus, according to the sol-gel method, long duration is especially required for gelation.

[0009] This invention is invented under such circumstances and aims at offering the approach for manufacturing the solid electrolyte of lithium ion conductivity in low temperature and a short time, the solid electrolyte manufactured by this, and a lithium cell equipped with such a solid electrolyte.

[0010]

[Means for Solving the Problem] According to the 1st side face of this invention, the manufacture approach of a solid electrolyte of having lithium ion conductivity including a lithium, titanium, Lynn, and oxygen is offered. This manufacture approach is characterized by heating the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply, and calcinating, without passing through a gelation process.

[0011] After such a manufacture approach of the solid electrolyte of a configuration forms the network of a configuration element by the solution system, by burning and hardening this, it is the technique of forming the predetermined crystal structure which comes to contain a lithium, titanium, Lynn, and oxygen, and does not pass through the intentional gelation process of a precursor solution on the occasion of network formation. Therefore, according to the approach concerned, the LISICON mold solid electrolyte expressed with the proximate composition type $LiM(PO4)$ 3 can be compounded, without passing through the gelation process which requires a long time. Moreover, in that the network of a configuration element is formed, the approach and sol-gel method concerning this invention do not need to pass through an elevated-temperature process like scorification by this invention in common by the solution system, either.

[0012] Conventionally, in the sol-gel method for compounding a solid electrolyte, the titanium alkoxide which is easy to hydrolyze is adopted as a titanium source of supply that a configuration element network should be formed by hydrolysis in an alcoholic solution system. The titanium alkoxide is comparatively unstable and it has the property to be easy to produce precipitate

according to these operations, under coexistence of a phosphoric acid (H3PO4) or its metal salt. In the process of composition of a solid electrolyte, if precipitate arises with a precursor solution, formation of the configuration element network of a suitable presentation will be checked, and the solid electrolyte of the purpose presentation cannot be obtained. Therefore, in a sol-gel method, in composition of a LISICON mold solid electrolyte, a phosphoric acid (H3PO4) or its metal salt cannot be used as the Lynn source of supply and an oxygen supply, but the quiet phosphoric-acid triethyl which does not act on a titanium alkoxide, tributyl phosphate, and ammonium phosphate are used as Lynn and an oxygen supply, for example. When using these quiet phosphoric-acids compound, in order to incorporate PO4 appropriately to a configuration element network, it is necessary to pass through the gelation process of the long duration by the hydrolysis carried out slowly. ** which has combined this with the oxygen atom of a phosphoric acid in the incorporation process of PO4 to a network -- it is thought that it is because PO4 needs to connect with a network through the oxygen atom concerned, high chemical species fully dissociating. Thus, especially in the sol-gel method for compounding the solid electrolyte of a LISICON mold, in order to incorporate PO4 suitable for a configuration element network with Ti, it is necessary to pass through the gelation process of the long duration by the hydrolysis carried out slowly.

[0013] On the other hand, the approach concerning the 1st side face of this invention does not pass through the gelation process for forming a configuration element network. The organic titanium compound of un-hydrolyzing nature is dissolving in the precursor solution used by this invention as a titanium source of supply, and the organic titanium compound concerned exists in stability comparatively by the predetermined solution system. Here, the organic titanium compound of un-hydrolyzing nature means the organic titanium compound which can hold the structure which checks the hydrolysis attack by the acid or bases to association near Ti, such as Ti-O-R association, for example until the configuration element network made into the purpose with a precursor solution is formed. As such an organic titanium compound, the dihydroxy titanium screw lactate expressed with the following chemical formula (1) and its derivative are mentioned, for example.

[0014]

[Formula 1]

$$\left[(OH)_2Ti-O-\underset{COO^-}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_3\right]_2\cdot 2H^+ \quad \cdots\cdots \quad (1)$$

[0015] Since association of the organic titanium compound concerned near the titanium is fully protected from the hydrolysis attack in the condition that the organic titanium compound of such un-hydrolyzing nature is dissolving in the precursor solution, the degree of freedom of usable chemical species is high about the other element source of supply which should be added in a precursor solution. It can be used even if it is the chemical species which act on titanium and are specifically easy to produce precipitate as a source of supply of other elements, such as a lithium, Lynn, and oxygen. Therefore, it also enables ** not to acquire a gelation process but to choose stable chemical species as extent in which network formation is possible from the chemical species of such titanium operation nature. Moreover, it is such stability and also it becomes possible by using an element source of supply for the organic titanium compound of un-hydrolyzing nature itself to originate in the stability, and not to acquire a gelation process, but to also incorporate ** appropriately in a network.

[0016] For example, if dihydroxy titanium screw lactate is adopted as an organic titanium compound which is a titanium source of supply when compounding a LISICON mold solid electrolyte, a phosphoric acid (H3PO4) or its metal salt can be used as Lynn and an oxygen supply. As for PO43- originating in a phosphoric acid or a phosphoric-acid metal salt, it is possible to exist in stability comparatively in a predetermined precursor solution system, and for a precursor solution not to gel, but for ** to also form a network appropriately with other

elements, such as titanium and a lithium.
[0017] Thus, according to the approach concerning the 1st side face of this invention, it sets in a precursor solution. By adopting the organic titanium compound of un-hydrolyzing nature as a titanium source of supply By burning and hardening this, after forming the network of a configuration element by the solution system, without **'s also being able to use the chemical species in which network formation is possible not through a gelation process as another element source of supply, consequently passing through a gelation process It is possible to form the solid electrolyte of lithium ion conductivity. Therefore, according to the approach concerning the 1st side face of this invention, the solid electrolyte of a LISICON mold etc. can be compounded, without passing through an elevated-temperature process like scorification, without passing through the gelation process which requires a long time.
[0018] The organic titanium compound as a titanium source of supply contained in the precursor solution of this invention is dihydroxy titanium screw lactate or a dihydroxy titanium screw lactate derivative preferably.
[0019] The precursor solution contains the phosphoric acid or the phosphoric-acid metal salt as the Lynn source of supply and an oxygen supply preferably. The precursor solution contains the acetic-acid lithium as a lithium source of supply preferably. Moreover, the precursor solution contains water as a solvent component preferably. In addition to water, the precursor solution contains alcohol as a solvent component more preferably.
[0020] Baking in this invention is performed above 560 degrees C whenever [stoving temperature]. Temporary baking is more preferably performed whenever [stoving temperature] before baking at less than 560 degrees C, for example, 250-400 degrees C. The solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen is a LISICON mold solid electrolyte preferably.
[0021] According to the 2nd side face of this invention, the solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen is offered. This solid electrolyte is characterized by having formed the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to the base material, having heated the coat concerned and being formed by calcinating without passing through a gelation process.
[0022] The solid electrolyte concerning the 2nd side face of this invention is formed by calcinating it, after applying the precursor solution same with being used in the approach concerning the 1st side face to a predetermined base material by spin coating, DIP coating, etc. Therefore, the effectiveness same with having mentioned above about the 1st side face in formation of a solid electrolyte is done so by the 2nd side face.
[0023] According to the 3rd side face of this invention, a lithium cell is offered. This lithium cell is characterized by having had the solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, and the solid electrolyte concerned having formed the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to the positive-electrode object and/or the negative-electrode object, and having heated the coat concerned and being formed by calcinating without passing through a gelation process.
[0024] The lithium cell concerning the 3rd side face of this invention is equipped with the solid electrolyte formed by calcinating it after applying the precursor solution same with being used in the approach concerning the 1st side face to a positive-electrode object or a negative-electrode object by spin coating, DIP coating, etc. Therefore, the effectiveness same with having mentioned above about the 1st side face in formation of a solid electrolyte is done so by the 3rd side face.
[0025]
[Embodiment of the Invention] Drawing 1 is a flow chart showing the manufacture approach of the solid electrolyte concerning the 1st operation gestalt of this invention. The solid electrolyte concerning this invention is a solid electrolyte of the LISICON mold in which lithium ion conductivity is shown including a lithium, titanium, Lynn, and oxygen at least as a configuration element.

[0026] In manufacture of the solid electrolyte of this operation gestalt, a precursor solution is first prepared in the precursor solution preparation process S1. As a solvent for constituting a precursor solution, the mixed solvent of water or water, and alcohol is used. As alcohol for constituting a mixed solvent, isopropanol and ethanol can be used, for example. The raw material containing the configuration element of the solid electrolyte of the synthetic purpose is added, and it is made to dissolve to these solvents [like] at the precursor solution preparation process S1. At this time, a precursor solution is prepared so that a configuration element may live together by the desired mole ratio. Moreover, in order to adjust the viscosity of the precursor solution concerned, polymeric materials, such as a polyethylene glycol, may be further added to a precursor solution as a thickener.
[0027] For example, in case a LISICON mold solid electrolyte is manufactured, as a lithium source of supply, an acetic-acid lithium, a lithium hydroxide, a lithium nitrate, and an oxalic acid lithium can be used, for example. As a titanium source of supply, dihydroxy titanium screw lactate and its derivative can be used, for example. As a Lynn source of supply, a phosphoric acid and its metal salt can be used, for example. If dihydroxy titanium screw lactate and its derivative are used as a titanium source of supply, it will be easy to form a uniform configuration element network at the time of synthetic completion. In addition, dihydroxy titanium screw lactate has comparatively high coexistence stability with PO43- of a phosphoric acid or the phosphoric-acid metal salt origin which is the Lynn source of supply, and is suitable to form a configuration element network, without passing through a gelation process. Moreover, in a precursor solution, In, Sc, Ga, Cr, aluminum, or Fe may be further added with the gestalt of a nitrate, a hydroxide, a nitrate, and an oxalate that the lithium ion conductivity of a solid electrolyte should be improved. By adding such an element in a precursor solution by suitable concentration, it is possible for network ****** to make the crystal structure incorporate the element concerned so that a part of Ti may be permuted.
[0028] Next, in the spreading process S2, the precursor solution prepared as mentioned above is applied on a predetermined base material, and the coat which consists of a precursor solution is formed to a base material. As a spreading means, spin coating, DIP coating, and spray coating are employable, for example. The thickness of a coat, as a result the thickness of a solid electrolyte thin film can be adjusted with the addition of a thickener. Finally by passing through such a spreading process, a thin solid electrolyte will be obtained. This process is not performed when there is no need of forming a solid electrolyte in a thin film.
[0029] Next, in the heating baking process S3, the precursor solution put into the precursor solution coat or the heat-resistant container on a base material is heated a base material or the heat-resistant whole container, and is calcinated at 560-1200 degrees C whenever [stoving temperature] for 1 to 5 hours. It can calcinate decomposing the diphosphorus pentaoxide which may be formed from the Lynn source of supply, after transpiring the solvent contained in the precursor solution, if 560 degrees C or more cost whenever [stoving temperature]. This invention may perform temporary baking of 1 - 2 hours at 250-400 degrees C before such a baking process. If such temporary baking is performed, it will become possible to be able to burn, before this baking of the organic compound kind included in each element source of supply, consequently to sinter a good solid electrolyte.
[0030] After passing through the above process, the solid electrolyte of lithium ion conductivity concerning this invention is obtained by cooling appropriately. Thus, according to this invention, the solid electrolyte of the lithium ion conductivity [sol-gel method / low temperature and] in a short-time process can be obtained from scorification. Such a solid electrolyte of lithium ion conductivity can be used as an ingredient for constituting the electrolyte layer of a lithium primary cell or a lithium secondary battery. Moreover, in this invention, a precursor solution is directly given to a baking process, and is not fully gelled before baking. Therefore, according to this invention, it becomes possible to be able to form a coat thin enough on a base material with a precursor solution, consequently to form the lithium ion conductivity solid-electrolyte membrane thin enough corresponding to the thickness. Such a thin lithium ion conductivity solid-electrolyte membrane is useful as an electrolyte layer of a lithium primary cell or a lithium secondary battery.

[0031] Drawing 2 is the sectional view of lithium cell X concerning the 2nd operation gestalt of this invention. As shown in drawing 2 , lithium cell X concerning this invention is equipped with the solid electrolyte layer 30 which intervenes between the positive-electrode object 10 which consists of a positive-electrode current collection layer 11 and a positive-electrode layer 12, the negative-electrode object 20 which consists of a negative-electrode current collection layer 21 and a negative-electrode layer 22, and the positive-electrode object 10 and the negative-electrode object 20. In this operation gestalt, the positive-electrode current collection layer 11 and the negative-electrode current collection layer 21 are being respectively fixed through the charge collector 43 to the positive-electrode can 41 and the negative-electrode can 42. The positive-electrode can 41, the negative-electrode can 42, and a charge collector 43 are for example, the products made from stainless steel. The closure of between the positive-electrode can 41 and the negative-electrode can 42 is carried out with the packing material 44 made from polypropylene. A charge collector 43 is for aiming at a flow, filling the opening between the positive-electrode current collection layer 11 and the positive-electrode can 41 and between the negative-electrode current collection layer 21 and the negative-electrode can 42. Thus, lithium cell X of this operation gestalt is constituted as a coin mold lithium secondary battery.
[0032] Respectively, the positive-electrode current collection layer 11 and the negative-electrode current collection layer 21 are for making it flow through the positive-electrode layer 12 and the negative-electrode layer 22 good to a predetermined terminal 41, i.e., a positive-electrode can, and the predetermined negative-electrode can 42, and are constituted by the high conductivity ingredient. For example, aluminum, copper, or nickel is formed vacuum evaporationo, sputtering, or by plating. Or you may constitute using the piece of stainless steel.
[0033] The positive-electrode layer 12 is constituted as a mixture of granular positive active material, a granular electric conduction agent, and the binder that consists of a resin ingredient.
[0034] A lithium-transition-metals multiple oxide can be used as positive active material. As a lithium-transition-metals multiple oxide, lithium nickel complex oxide ($LiNiO_2$), a lithium-manganese multiple oxide ($LiMnO_2$), a lithium-cobalt multiple oxide ($LiCoO_2$), etc. are mentioned, for example. Or the lithium-nickel system multiple oxide by which some nickel in lithium nickel complex oxide ($LiNiO_2$) is permuted by other elements as positive active material can also be used.
[0035] As an electric conduction agent for forming the positive-electrode layer 12, acetylene black, graphite, carbon, etc. are mentioned, for example. Moreover, as a binder for forming the positive-electrode layer 12, polyethylene oxide, an ethylene-propylene-diene ternary polymerization object, etc. are mentioned, for example.
[0036] The negative-electrode layer 22 is constituted as a mixture of a granular negative-electrode active material, a granular electric conduction agent, and the binder that consists of a resin ingredient.
[0037] As a negative-electrode active material, lithium alloys, such as lithium-transition-metals multiple oxides, such as lithium titanate and a banazin san lithium, and a lithium-aluminium alloy, a lithium-indium alloy, etc. are mentioned, for example. Moreover, a carbon material may be used as a negative-electrode active material. As a carbon material, graphite, conjugated-system resin (for example, phenol resin, acrylic resin, polyimide resin, polyamide resin), a condensed multi-ring hydrocarbon compound (for example, naphthalene, a phenanthrene, an anthracene), and furan resin (for example, furfuryl alcohol, the homopolymers of FURIRARU, and these copolymers) are mentioned, for example. These carbon materials may be independent, or two or more sorts may be mixed and used, and especially graphite is used suitably.
[0038] Having mentioned above about the positive-electrode layer 12 as the electric conduction agent and binder for forming the negative-electrode layer 22 and the same thing can be used.
[0039] The solid electrolyte layer 30 is constituted by the inorganic solid electrolyte which has lithium ion conductivity. The solid electrolyte layer 30 is the solid electrolyte of the LISICON mold formed by the manufacture approach of the solid electrolyte concerning the 1st operation gestalt. In formation of the solid electrolyte layer 30, DIP coating of the precursor solution mentioned above about the 1st operation gestalt is first carried out to the positive-electrode layer 12 or the negative-electrode layer 22 formed in the manufacture process of lithium cell X.

Next, it calcinates at 560-1200 degrees C whenever [stoving temperature] by heat-treatment for 1 to 5 hours. Before a baking process, temporary baking of 1 - 2 hours may be performed at 250-400 degrees C. By repeating from such DIP coating to baking the number of predetermined times, the solid electrolyte layer 30 of desired thickness can be formed on the positive-electrode layer 12 or the negative-electrode layer 22. In this operation gestalt, it is formed by well-known technique about other parts of lithium cell X.

[0040] Although lithium cell X of this operation gestalt is constituted as a coin mold, about the lithium cell concerning this invention, any gestalt of cylindrical, a square shape, and a sheet mold can be used for it.

[0041]

[Example] Next, the example of this invention is indicated.

[0042] To the water solution which contains the phosphoric acid (H_3PO_4, product made from the Wako Pure Chem industry) as a <preparation of precursor solution> Lynn source of supply by 10wt(s)% concentration, it added and the acetic-acid lithium (product made from the Wako Pure Chem industry) as a lithium source of supply was mixed so that a lithium and the abundance ratio of Lynn might be set to 1:3 (mole ratio). Next, the sol-like precursor solution was prepared by adding the water solution prepared as mentioned above to the dihydroxy titanium screw lactate solution (trade name: ORUGACHIKKUSU TC-310, Matsumoto Chemical Industry make) containing the dihydroxy titanium screw lactate as a titanium source of supply, so that a lithium, titanium, and the abundance ratio of Lynn may be set to 1:2:3 (mole ratio), and mixing this for 1 minute at 23 degrees C. The dihydroxy titanium screw lactate solution used by this example consists of the dihydroxy titanium screw lactate 43 weight section, the water 17 weight section, and the isopropanol 40 weight section.

[0043] The precursor solution which is a <formation of solid-electrolyte membrane> ****, and was made and prepared was applied on the quartz-glass substrate (40mmx40mm) by spin coating. At this time, the rotation conditions of a quartz-glass substrate were set as for 10 seconds by 500rpm for 10 seconds following this by 100rpm. Next, the substrate with which it did in this way and the precursor solution coat was formed was put into the electric furnace, and it calcinated by heating at 800 degrees C under an atmospheric-air ambient atmosphere for 5 hours. Then, the substrate was picked out from the electric furnace and cooled radiationally. Thus, the thin film-like solid electrolyte was able to be formed on the quartz-glass substrate.

[0044] Thus, about the formed solid electrolyte thin film, when analyzed chemically by ICP emission spectral analysis, it turned out that the lithium which constitutes the solid electrolyte concerned, titanium, and the mole ratio of Lynn deal with the each element's in precursor solution existence mole ratio (1:2:3). Moreover, when analysis by the X diffraction was performed about this solid electrolyte thin film, the diffraction pattern showed that a crystal phase was a compound expressed with $LiTi_2(PO_4)_3$. Furthermore, it was 0.3 micrometers when thickness was measured by the contact mold thickness gage about this solid electrolyte thin film. According to this example the above result, in the solid electrolyte thin film of a LISICON mold, it is low temperature from scorification, and scorification and a sol-gel method showed that it was compoundable in a short time. Moreover, according to this example, when adding the thickener of optimum dose to the precursor solution, the thickness was understood are controllable to micrometer order.

[0045] As the above conclusion, it enumerates as an additional remark below about the configuration of this invention, and its variation.

[0046] (Additional remark 1) The manufacture approach of a solid electrolyte characterized by calcinating the precursor solution which is the manufacture approach of a solid electrolyte of having lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, and contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply, without passing through a gelation process.

(Additional remark 2) Said organic titanium compound is the manufacture approach of a solid electrolyte given in the additional remark 1 which is dihydroxy titanium screw lactate or a dihydroxy titanium screw lactate derivative.

(Additional remark 3) Said precursor solution is the manufacture approach of a solid electrolyte

given in the additional remarks 1 or 2 containing a phosphoric acid or a phosphoric-acid metal salt as the Lynn source of supply and an oxygen supply.
(Additional remark 4) Said precursor solution is the manufacture approach of the solid electrolyte any one publication of three from the additional remark 1 which contains an acetic-acid lithium as a lithium source of supply.
(Additional remark 5) Said precursor solution is the manufacture approach of the solid electrolyte any one publication of four from the additional remark 1 which contains water as a solvent component.
(Additional remark 6) Said precursor solution is the manufacture approach of a solid electrolyte given in the additional remark 5 which contains alcohol as a solvent component.
(Additional remark 7) Whenever [in said baking / stoving temperature] is the manufacture approach of the solid electrolyte any one publication of six from the additional remark 1 which is 560 degrees C or more.
(Additional remark 8) The manufacture approach of a solid electrolyte given in the additional remark 7 which performs temporary baking at 250-400 degrees C whenever [stoving temperature] before said baking.
(Additional remark 9) Said solid electrolyte is the manufacture approach of the solid electrolyte any one publication of eight from the additional remark 1 which is a LISICON mold solid electrolyte.
(Additional remark 10) The solid electrolyte which is a solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, forms the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to a base material, heats the coat concerned, and is characterized by being formed by calcinating without passing through a gelation process.
It is a lithium cell equipped with the solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen. (Additional remark 11) Said solid electrolyte The lithium cell which forms the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to a positive-electrode object and/or a negative-electrode object, heats the coat concerned, and is characterized by being formed by calcinating without passing through a gelation process.
[0047]
[Effect of the Invention] According to this invention, it is low temperature from scorification, and the solid electrolyte of lithium ion conductivity can be compounded rather than scorification or a sol-gel method in a short time. Furthermore, according to this invention, thin film formation to micrometer order is possible in a lithium ion conductivity solid electrolyte.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacture approach of a solid electrolyte of having lithium ion conductivity, the solid electrolyte manufactured by this, and a lithium cell.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Since it has the features of it being lightweight and having a high energy consistency, a lithium cell is used in many cases as the memory maintenance power sources in pocket electronic equipment and drive power sources, such as a cellular phone and a notebook computer. A lithium cell is equipped with the electrolyte which generally permits migration of a lithium ion between the positive electrode which comes to include a lithium ion the positive active material in which charge and discharge are possible, the negative electrode which comes to contain negative-electrode active materials, such as an ingredient in which a dope and a dedope of a lithium are possible, and a lithium alloy, and a positive electrode and a negative electrode, and is constituted as a rechargeable battery.
[0003] To the lithium secondary battery, the demand of thin-shape-izing and the further formation of a high energy consistency is increasing with the formation of small lightweight of a portable information device etc. in recent years. Although the nonaqueous electolyte of lithium ion conductivity was generally conventionally used as an electrolyte of a lithium secondary battery, in recent years, the solid electrolyte attracts attention that it should correspond to the demand of thin-shape-izing of a lithium secondary battery, and the formation of a high energy consistency.
[0004] As a solid electrolyte, the gel electrolyte, the intrinsic polymer electrolyte, and the inorganic solid electrolyte are known. In the lithium cell, since it cannot need reinforcing materials, can function also as an inter-electrode separator, and does not produce a liquid spill, even if it thin-film-izes it, since an inorganic solid electrolyte is high intensity and it has the advantage that safety is high, it attracts attention especially as a solid electrolyte of a lithium cell application.
[0005] As an inorganic solid electrolyte in which lithium ion conductivity is shown, the glass of a Li3N single crystal and LiI-Li2 S-P2S5 system, LiI-Li2S2-B-2S3 system, and LiI-Li2 S-SiS4 system is known conventionally. However, since these ingredients are chemical and thermally unstable, they are not practical as an electrolyte of a lithium cell.
[0006] Then, research of the oxide solid electrolyte of a crystallized glass system is active in recent years as an inorganic solid electrolyte in which lithium ion conductivity is shown. As a typical thing, the thing of a LISICON mold expressed with the proximate composition type LiM (PO4) 3 (M=Ti, Zr, germanium, Hf) is mentioned. Generally in the oxide solid electrolyte of a LISICON mold, improvement in lithium ion conductivity is achieved by carrying out the element permutation of a part of M. For example, in Li1+XAlXTi2-X (PO4)3 by which Ti is chosen as M in the proximate composition type of upper **, and a part of Ti concerned is permuted with aluminum, it is possible to attain high ion conductivity called 7x10-4 S/cm at a room temperature. Such a crystallized glass system oxide solid electrolyte is comparatively stable chemically and thermally, and useful as a solid electrolyte of a lithium cell. The lithium secondary battery equipped with the oxide solid electrolyte of such a LISICON mold is indicated by JP,2002-42876,A.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, it is low temperature from scorification, and the solid electrolyte of lithium ion conductivity can be compounded rather than scorification or a sol-gel method in a short time. Furthermore, according to this invention, thin film formation to micrometer order is possible in a lithium ion conductivity solid electrolyte.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In manufacture of inorganic solid electrolytes, such as an oxide solid electrolyte, scorification or a sol-gel method is adopted conventionally. Scorification is the technique of cooling this and forming the predetermined crystal structure, after forming the network of a configuration element according to solid phase reaction. Therefore, in order to intercrystallize a raw material, very a lot of heat is needed. Moreover, since advance of solid phase reaction is slow, the conclusion of a reaction takes long duration. In manufacture of a LISICON mold solid electrolyte, the raw material mixture which consists of each powdery element source of supply is heated and fused to an about 1500-degree C elevated temperature for example first. After maintaining a melting condition for 1 to 2 hours, whenever [stoving temperature] is lowered, and it considers as the condition of the solid solution thru/or a solid-state, and heats at about 800 degrees C for 12 hours or more. Then, a temperature up is carried out again and it heats above 1000 degrees C for 24 hours, and this is cooled and the target solid electrolyte is obtained. Thus, in order to obtain a solid electrolyte with scorification, great heat and time amount are needed. In addition, it is difficult to compound a solid electrolyte massive according to scorification, and to form the solid electrolyte thin film of the thickness of micrometer order from the massive object concerned.
[0008] On the other hand, a sol-gel method is the technique of burning and hardening this and forming the predetermined crystal structure, after forming the network of a configuration element by the hydrolysis reaction in a solution system. Therefore, an elevated-temperature process like scorification is not needed. However, in order to form a suitable network, by advancing hydrolysis slowly on quiet conditions, it must gel through a sol condition about a raw material solution, and a long time is required rather than scorification. In manufacture of a LISICON mold solid electrolyte, the alcoholic solution containing each element source of supply is first solated at 25-80 degrees C, for example. Next, the sol concerned is left one day to about one week, and is made to gel at 25-120 degrees C. Then, heating baking of about 1 hour is performed at 800-900 degrees C, this is cooled and the target solid electrolyte is obtained. Thus, according to the sol-gel method, long duration is especially required for gelation.
[0009] This invention is invented under such circumstances and aims at offering the approach for manufacturing the solid electrolyte of lithium ion conductivity in low temperature and a short time, the solid electrolyte manufactured by this, and a lithium cell equipped with such a solid electrolyte.

[Translation done.]

MEANS

[Means for Solving the Problem] According to the 1st side face of this invention, the manufacture approach of a solid electrolyte of having lithium ion conductivity including a lithium, titanium, Lynn, and oxygen is offered. This manufacture approach is characterized by heating the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply, and calcinating, without passing through a gelation process.
[0011] After such a manufacture approach of the solid electrolyte of a configuration forms the network of a configuration element by the solution system, by burning and hardening this, it is the technique of forming the predetermined crystal structure which comes to contain a lithium, titanium, Lynn, and oxygen, and does not pass through the intentional gelation process of a precursor solution on the occasion of network formation. Therefore, according to the approach concerned, the LISICON mold solid electrolyte expressed with the proximate composition type LiM(PO4) 3 can be compounded, without passing through the gelation process which requires a long time. Moreover, in that the network of a configuration element is formed, the approach and sol-gel method concerning this invention do not need to pass through an elevated-temperature process like scorification by this invention in common by the solution system, either.
[0012] Conventionally, in the sol-gel method for compounding a solid electrolyte, the titanium alkoxide which is easy to hydrolyze is adopted as a titanium source of supply that a configuration element network should be formed by hydrolysis in an alcoholic solution system. The titanium alkoxide is comparatively unstable and it has the property to be easy to produce precipitate according to these operations, under coexistence of a phosphoric acid (H3PO4) or its metal salt. In the process of composition of a solid electrolyte, if precipitate arises with a precursor solution, formation of the configuration element network of a suitable presentation will be checked, and the solid electrolyte of the purpose presentation cannot be obtained. Therefore, in a sol-gel method, in composition of a LISICON mold solid electrolyte, a phosphoric acid (H3PO4) or its metal salt cannot be used as the Lynn source of supply and an oxygen supply, but the quiet phosphoric-acid triethyl which does not act on a titanium alkoxide, tributyl phosphate, and ammonium phosphate are used as Lynn and an oxygen supply, for example. When using these quiet phosphoric-acids compound, in order to incorporate PO4 appropriately to a configuration element network, it is necessary to pass through the gelation process of the long duration by the hydrolysis carried out slowly. ** which has combined this with the oxygen atom of a phosphoric acid in the incorporation process of PO4 to a network -- it is thought that it is because PO4 needs to connect with a network through the oxygen atom concerned, high chemical species fully dissociating. Thus, especially in the sol-gel method for compounding the solid electrolyte of a LISICON mold, in order to incorporate PO4 suitable for a configuration element network with Ti, it is necessary to pass through the gelation process of the long duration by the hydrolysis carried out slowly.
[0013] On the other hand, the approach concerning the 1st side face of this invention does not pass through the gelation process for forming a configuration element network. The organic titanium compound of un-hydrolyzing nature is dissolving in the precursor solution used by this invention as a titanium source of supply, and the organic titanium compound concerned exists in stability comparatively by the predetermined solution system. Here, the organic titanium

compound of un-hydrolyzing nature means the organic titanium compound which can hold the structure which checks the hydrolysis attack by the acid or bases to association near Ti, such as Ti-O-R association, for example until the configuration element network made into the purpose with a precursor solution is formed. As such an organic titanium compound, the dihydroxy titanium screw lactate expressed with the following chemical formula (1) and its derivative are mentioned, for example.
[0014]
[Formula 1]

$$\left| (OH)_2Ti-O-\overset{\displaystyle H}{\underset{\displaystyle COO^-}{C}}-CH_3 \right|_2 \cdot 2H^+ \quad \text{------} \quad (1)$$

[0015] Since association of the organic titanium compound concerned near the titanium is fully protected from the hydrolysis attack in the condition that the organic titanium compound of such un-hydrolyzing nature is dissolving in the precursor solution, the degree of freedom of usable chemical species is high about the other element source of supply which should be added in a precursor solution. It can be used even if it is the chemical species which act on titanium and are specifically easy to produce precipitate as a source of supply of other elements, such as a lithium, Lynn, and oxygen. Therefore, it also enables ** not to acquire a gelation process but to choose stable chemical species as extent in which network formation is possible from the chemical species of such titanium operation nature. Moreover, it is such stability and also it becomes possible by using an element source of supply for the organic titanium compound of un-hydrolyzing nature itself to originate in the stability, and not to acquire a gelation process, but to also incorporate ** appropriately in a network.
[0016] For example, if dihydroxy titanium screw lactate is adopted as an organic titanium compound which is a titanium source of supply when compounding a LISICON mold solid electrolyte, a phosphoric acid (H3PO4) or its metal salt can be used as Lynn and an oxygen supply. As for PO43- originating in a phosphoric acid or a phosphoric-acid metal salt, it is possible to exist in stability comparatively in a predetermined precursor solution system, and for a precursor solution not to gel, but for ** to also form a network appropriately with other elements, such as titanium and a lithium.
[0017] Thus, according to the approach concerning the 1st side face of this invention, it sets in a precursor solution. By adopting the organic titanium compound of un-hydrolyzing nature as a titanium source of supply By burning and hardening this, after forming the network of a configuration element by the solution system, without **'s also being able to use the chemical species in which network formation is possible not through a gelation process as another element source of supply, consequently passing through a gelation process It is possible to form the solid electrolyte of lithium ion conductivity. Therefore, according to the approach concerning the 1st side face of this invention, the solid electrolyte of a LISICON mold etc. can be compounded, without passing through an elevated-temperature process like scorification, without passing through the gelation process which requires a long time.
[0018] The organic titanium compound as a titanium source of supply contained in the precursor solution of this invention is dihydroxy titanium screw lactate or a dihydroxy titanium screw lactate derivative preferably.
[0019] The precursor solution contains the phosphoric acid or the phosphoric-acid metal salt as the Lynn source of supply and an oxygen supply preferably. The precursor solution contains the acetic-acid lithium as a lithium source of supply preferably. Moreover, the precursor solution contains water as a solvent component preferably. In addition to water, the precursor solution contains alcohol as a solvent component more preferably.
[0020] Baking in this invention is performed above 560 degrees C whenever [stoving temperature]. Temporary baking is more preferably performed whenever [stoving temperature] before baking at less than 560 degrees C, for example, 250-400 degrees C. The solid electrolyte

which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen is a LISICON mold solid electrolyte preferably.
[0021] According to the 2nd side face of this invention, the solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen is offered. This solid electrolyte is characterized by having formed the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to the base material, having heated the coat concerned and being formed by calcinating without passing through a gelation process.
[0022] The solid electrolyte concerning the 2nd side face of this invention is formed by calcinating it, after applying the precursor solution same with being used in the approach concerning the 1st side face to a predetermined base material by spin coating, DIP coating, etc. Therefore, the effectiveness same with having mentioned above about the 1st side face in formation of a solid electrolyte is done so by the 2nd side face.
[0023] According to the 3rd side face of this invention, a lithium cell is offered. This lithium cell is characterized by having had the solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, and the solid electrolyte concerned having formed the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to the positive-electrode object and/or the negative-electrode object, and having heated the coat concerned and being formed by calcinating without passing through a gelation process.
[0024] The lithium cell concerning the 3rd side face of this invention is equipped with the solid electrolyte formed by calcinating it after applying the precursor solution same with being used in the approach concerning the 1st side face to a positive-electrode object or a negative-electrode object by spin coating, DIP coating, etc. Therefore, the effectiveness same with having mentioned above about the 1st side face in formation of a solid electrolyte is done so by the 3rd side face.
[0025]
[Embodiment of the Invention] Drawing 1 is a flow chart showing the manufacture approach of the solid electrolyte concerning the 1st operation gestalt of this invention. The solid electrolyte concerning this invention is a solid electrolyte of the LISICON mold in which lithium ion conductivity is shown including a lithium, titanium, Lynn, and oxygen at least as a configuration element.
[0026] In manufacture of the solid electrolyte of this operation gestalt, a precursor solution is first prepared in the precursor solution preparation process S1. As a solvent for constituting a precursor solution, the mixed solvent of water or water, and alcohol is used. As alcohol for constituting a mixed solvent, isopropanol and ethanol can be used, for example. The raw material containing the configuration element of the solid electrolyte of the synthetic purpose is added, and it is made to dissolve to these solvents [like] at the precursor solution preparation process S1. At this time, a precursor solution is prepared so that a configuration element may live together by the desired mole ratio. Moreover, in order to adjust the viscosity of the precursor solution concerned, polymeric materials, such as a polyethylene glycol, may be further added to a precursor solution as a thickener.
[0027] For example, in case a LISICON mold solid electrolyte is manufactured, as a lithium source of supply, an acetic-acid lithium, a lithium hydroxide, a lithium nitrate, and an oxalic acid lithium can be used, for example. As a titanium source of supply, dihydroxy titanium screw lactate and its derivative can be used, for example. As a Lynn source of supply, a phosphoric acid and its metal salt can be used, for example. If dihydroxy titanium screw lactate and its derivative are used as a titanium source of supply, it will be easy to form a uniform configuration element network at the time of synthetic completion. In addition, dihydroxy titanium screw lactate has comparatively high coexistence stability with PO43- of a phosphoric acid or the phosphoric-acid metal salt origin which is the Lynn source of supply, and is suitable to form a configuration element network, without passing through a gelation process. Moreover, in a precursor solution, In, Sc, Ga, Cr, aluminum, or Fe may be further added with the gestalt of a nitrate, a hydroxide, a nitrate, and an oxalate that the lithium ion conductivity of a solid

electrolyte should be improved. By adding such an element in a precursor solution by suitable concentration, it is possible for network ****** to make the crystal structure incorporate the element concerned so that a part of Ti may be permuted.
[0028] Next, in the spreading process S2, the precursor solution prepared as mentioned above is applied on a predetermined base material, and the coat which consists of a precursor solution is formed to a base material. As a spreading means, spin coating, DIP coating, and spray coating are employable, for example. The thickness of a coat, as a result the thickness of a solid electrolyte thin film can be adjusted with the addition of a thickener. Finally by passing through such a spreading process, a thin solid electrolyte will be obtained. This process is not performed when there is no need of forming a solid electrolyte in a thin film.
[0029] Next, in the heating baking process S3, the precursor solution put into the precursor solution coat or the heat-resistant container on a base material is heated a base material or the heat-resistant whole container, and is calcinated at 560-1200 degrees C whenever [stoving temperature] for 1 to 5 hours. It can calcinate decomposing the diphosphorus pentaoxide which may be formed from the Lynn source of supply, after transpiring the solvent contained in the precursor solution, if 560 degrees C or more cost whenever [stoving temperature]. This invention may perform temporary baking of 1 - 2 hours at 250-400 degrees C before such a baking process. If such temporary baking is performed, it will become possible to be able to burn, before this baking of the organic compound kind included in each element source of supply, consequently to sinter a good solid electrolyte.
[0030] After passing through the above process, the solid electrolyte of lithium ion conductivity concerning this invention is obtained by cooling appropriately. Thus, according to this invention, the solid electrolyte of the lithium ion conductivity [sol-gel method / low temperature and] in a short-time process can be obtained from scorification. Such a solid electrolyte of lithium ion conductivity can be used as an ingredient for constituting the electrolyte layer of a lithium primary cell or a lithium secondary battery. Moreover, in this invention, a precursor solution is directly given to a baking process, and is not fully gelled before baking. Therefore, according to this invention, it becomes possible to be able to form a coat thin enough on a base material with a precursor solution, consequently to form the lithium ion conductivity solid-electrolyte membrane thin enough corresponding to the thickness. Such a thin lithium ion conductivity solid-electrolyte membrane is useful as an electrolyte layer of a lithium primary cell or a lithium secondary battery.
[0031] Drawing 2 is the sectional view of lithium cell X concerning the 2nd operation gestalt of this invention. As shown in drawing 2 , lithium cell X concerning this invention is equipped with the solid electrolyte layer 30 which intervenes between the positive-electrode object 10 which consists of a positive-electrode current collection layer 11 and a positive-electrode layer 12, the negative-electrode object 20 which consists of a negative-electrode current collection layer 21 and a negative-electrode layer 22, and the positive-electrode object 10 and the negative-electrode object 20. In this operation gestalt, the positive-electrode current collection layer 11 and the negative-electrode current collection layer 21 are being respectively fixed through the charge collector 43 to the positive-electrode can 41 and the negative-electrode can 42. The positive-electrode can 41, the negative-electrode can 42, and a charge collector 43 are for example, the products made from stainless steel. The closure of between the positive-electrode can 41 and the negative-electrode can 42 is carried out with the packing material 44 made from polypropylene. A charge collector 43 is for aiming at a flow, filling the opening between the positive-electrode current collection layer 11 and the positive-electrode can 41 and between the negative-electrode current collection layer 21 and the negative-electrode can 42. Thus, lithium cell X of this operation gestalt is constituted as a coin mold lithium secondary battery.
[0032] Respectively, the positive-electrode current collection layer 11 and the negative-electrode current collection layer 21 are for making it flow through the positive-electrode layer 12 and the negative-electrode layer 22 good to a predetermined terminal 41, i.e., a positive-electrode can, and the predetermined negative-electrode can 42, and are constituted by the high conductivity ingredient. For example, aluminum, copper, or nickel is formed vacuum evaporationo, sputtering, or by plating. Or you may constitute using the piece of stainless steel.

[0033] The positive-electrode layer 12 is constituted as a mixture of granular positive active material, a granular electric conduction agent, and the binder that consists of a resin ingredient.
[0034] A lithium-transition-metals multiple oxide can be used as positive active material. As a lithium-transition-metals multiple oxide, lithium nickel complex oxide (LiNiO2), a lithium-manganese multiple oxide (LiMnO2), a lithium-cobalt multiple oxide (LiCoO2), etc. are mentioned, for example. Or the lithium-nickel system multiple oxide by which some nickel in lithium nickel complex oxide (LiNiO2) is permuted by other elements as positive active material can also be used.
[0035] As an electric conduction agent for forming the positive-electrode layer 12, acetylene black, graphite, carbon, etc. are mentioned, for example. Moreover, as a binder for forming the positive-electrode layer 12, polyethylene oxide, an ethylene-propylene-diene ternary polymerization object, etc. are mentioned, for example.
[0036] The negative-electrode layer 22 is constituted as a mixture of a granular negative-electrode active material, a granular electric conduction agent, and the binder that consists of a resin ingredient.
[0037] As a negative-electrode active material, lithium alloys, such as lithium-transition-metals multiple oxides, such as lithium titanate and a banazin san lithium, and a lithium-aluminium alloy, a lithium-indium alloy, etc. are mentioned, for example. Moreover, a carbon material may be used as a negative-electrode active material. As a carbon material, graphite, conjugated-system resin (for example, phenol resin, acrylic resin, polyimide resin, polyamide resin), a condensed multi-ring hydrocarbon compound (for example, naphthalene, a phenanthrene, an anthracene), and furan resin (for example, furfuryl alcohol, the homopolymers of FURIRARU, and these copolymers) are mentioned, for example. These carbon materials may be independent, or two or more sorts may be mixed and used, and especially graphite is used suitably.
[0038] Having mentioned above about the positive-electrode layer 12 as the electric conduction agent and binder for forming the negative-electrode layer 22 and the same thing can be used.
[0039] The solid electrolyte layer 30 is constituted by the inorganic solid electrolyte which has lithium ion conductivity. The solid electrolyte layer 30 is the solid electrolyte of the LISICON mold formed by the manufacture approach of the solid electrolyte concerning the 1st operation gestalt. In formation of the solid electrolyte layer 30, DIP coating of the precursor solution mentioned above about the 1st operation gestalt is first carried out to the positive-electrode layer 12 or the negative-electrode layer 22 formed in the manufacture process of lithium cell X. Next, it calcinates at 560-1200 degrees C whenever [stoving temperature] by heat-treatment for 1 to 5 hours. Before a baking process, temporary baking of 1 - 2 hours may be performed at 250-400 degrees C. By repeating from such DIP coating to baking the number of predetermined times, the solid electrolyte layer 30 of desired thickness can be formed on the positive-electrode layer 12 or the negative-electrode layer 22. In this operation gestalt, it is formed by well-known technique about other parts of lithium cell X.
[0040] Although lithium cell X of this operation gestalt is constituted as a coin mold, about the lithium cell concerning this invention, any gestalt of cylindrical, a square shape, and a sheet mold can be used for it.

[Translation done.]

EXAMPLE

[Example] Next, the example of this invention is indicated.
[0042] To the water solution which contains the phosphoric acid (H_3PO_4, product made from the Wako Pure Chem industry) as a <preparation of precursor solution> Lynn source of supply by 10wt(s)% concentration, it added and the acetic-acid lithium (product made from the Wako Pure Chem industry) as a lithium source of supply was mixed so that a lithium and the abundance ratio of Lynn might be set to 1:3 (mole ratio). Next, the sol-like precursor solution was prepared by adding the water solution prepared as mentioned above to the dihydroxy titanium screw lactate solution (trade name: ORUGACHIKKUSU TC-310, Matsumoto Chemical Industry make) containing the dihydroxy titanium screw lactate as a titanium source of supply, so that a lithium, titanium, and the abundance ratio of Lynn may be set to 1:2:3 (mole ratio), and mixing this for 1 minute at 23 degrees C. The dihydroxy titanium screw lactate solution used by this example consists of the dihydroxy titanium screw lactate 43 weight section, the water 17 weight section, and the isopropanol 40 weight section.
[0043] The precursor solution which is a <formation of solid-electrolyte membrane> ****, and was made and prepared was applied on the quartz-glass substrate (40mmx40mm) by spin coating. At this time, the rotation conditions of a quartz-glass substrate were set as for 10 seconds by 500rpm for 10 seconds following this by 100rpm. Next, the substrate with which it did in this way and the precursor solution coat was formed was put into the electric furnace, and it calcinated by heating at 800 degrees C under an atmospheric-air ambient atmosphere for 5 hours. Then, the substrate was picked out from the electric furnace and cooled radiationally. Thus, the thin film-like solid electrolyte was able to be formed on the quartz-glass substrate.
[0044] Thus, about the formed solid electrolyte thin film, when analyzed chemically by ICP emission spectral analysis, it turned out that the lithium which constitutes the solid electrolyte concerned, titanium, and the mole ratio of Lynn deal with the each element's in precursor solution existence mole ratio (1:2:3). Moreover, when analysis by the X diffraction was performed about this solid electrolyte thin film, the diffraction pattern showed that a crystal phase was a compound expressed with $LiTi_2(PO_4)_3$. Furthermore, it was 0.3 micrometers when thickness was measured by the contact mold thickness gage about this solid electrolyte thin film. According to this example the above result, in the solid electrolyte thin film of a LISICON mold, it is low temperature from scorification, and scorification and a sol-gel method showed that it was compoundable in a short time. Moreover, according to this example, when adding the thickener of optimum dose to the precursor solution, the thickness was understood are controllable to micrometer order.
[0045] As the above conclusion, it enumerates as an additional remark below about the configuration of this invention, and its variation.
[0046] (Additional remark 1) The manufacture approach of a solid electrolyte characterized by calcinating the precursor solution which is the manufacture approach of a solid electrolyte of having lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, and contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply, without passing through a gelation process.
(Additional remark 2) Said organic titanium compound is the manufacture approach of a solid

electrolyte given in the additional remark 1 which is dihydroxy titanium screw lactate or a dihydroxy titanium screw lactate derivative.
(Additional remark 3) Said precursor solution is the manufacture approach of a solid electrolyte given in the additional remarks 1 or 2 containing a phosphoric acid or a phosphoric-acid metal salt as the Lynn source of supply and an oxygen supply.
(Additional remark 4) Said precursor solution is the manufacture approach of the solid electrolyte any one publication of three from the additional remark 1 which contains an acetic-acid lithium as a lithium source of supply.
(Additional remark 5) Said precursor solution is the manufacture approach of the solid electrolyte any one publication of four from the additional remark 1 which contains water as a solvent component.
(Additional remark 6) Said precursor solution is the manufacture approach of a solid electrolyte given in the additional remark 5 which contains alcohol as a solvent component.
(Additional remark 7) Whenever [in said baking / stoving temperature] is the manufacture approach of the solid electrolyte any one publication of six from the additional remark 1 which is 560 degrees C or more.
(Additional remark 8) The manufacture approach of a solid electrolyte given in the additional remark 7 which performs temporary baking at 250-400 degrees C whenever [stoving temperature] before said baking.
(Additional remark 9) Said solid electrolyte is the manufacture approach of the solid electrolyte any one publication of eight from the additional remark 1 which is a LISICON mold solid electrolyte.
(Additional remark 10) The solid electrolyte which is a solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen, forms the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to a base material, heats the coat concerned, and is characterized by being formed by calcinating without passing through a gelation process.
It is a lithium cell equipped with the solid electrolyte which has lithium ion conductivity including a lithium, titanium, Lynn, and oxygen. (Additional remark 11) Said solid electrolyte The lithium cell which forms the coat by the precursor solution which contains the organic titanium compound of un-hydrolyzing nature as a titanium source of supply to a positive-electrode object and/or a negative-electrode object, heats the coat concerned, and is characterized by being formed by calcinating without passing through a gelation process.

[Translation done.]

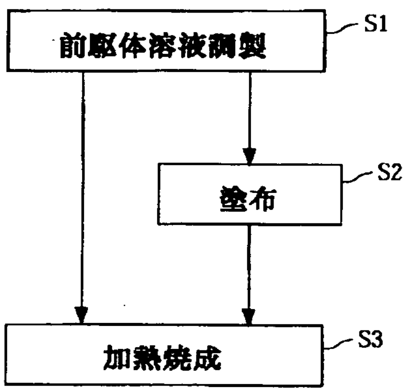
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is a flow chart about the manufacture approach of the solid electrolyte concerning this invention.
[Drawing 2] It is the sectional view of the lithium cell concerning this invention formed as a coin mold.
[Description of Notations]
S1 Precursor solution preparation process
S2 Spreading process
S3 Heating baking process
10 Positive-Electrode Object
11 Positive-Electrode Current Collection Layer
12 Positive-Electrode Layer
20 Negative-Electrode Object
21 Negative-Electrode Current Collection Layer
22 Negative-Electrode Layer
30 Solid Electrolyte Layer

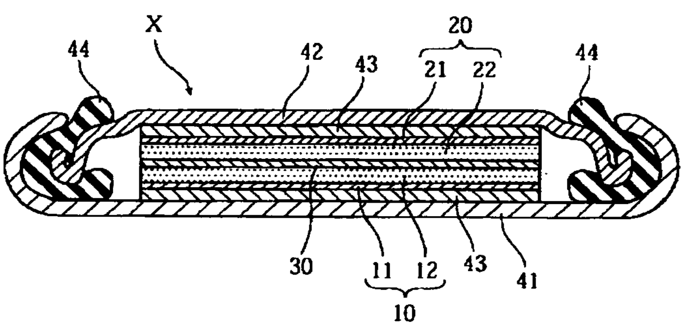
[Translation done.]

DRAWINGS

[Drawing 1]
本発明の固体電解質製造方法のフローチャート



[Drawing 2]
本発明のリチウム電池



[Translation done.]

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(71)出願人　000005223
富士通株式会社
神奈川県川崎市中原区上小田中４丁目１番１号
(72)発明者　吉田　賢介
神奈川県川崎市中原区上小田中４丁目１番１号　富士通株式会社内
(72)発明者　吉田　宏章
神奈川県川崎市中原区上小田中４丁目１番１号　富士通株式会社内
(74)代理人　100086380
弁理士　吉田　稔　（外２名）

最終頁に続く

(54)【発明の名称】　固体電解質の製造方法、固体電解質、およびリチウム電池

(57)【要約】
【課題】　リチウムイオン伝導性の固体電解質を低温かつ短時間で製造するための方法、これにより製造される固体電解質、および、そのような固体電解質を備えるリチウム電池を提供すること。
【課題手段】　リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質の製造方法において、チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液を加熱して、ゲル化工程を経ずに焼成することとする。

【特許請求の範囲】

【請求項１】　リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質の製造方法であって、

チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液を加熱して、ゲル化工程を経ずに焼成することを特徴とする、固体電解質の製造方法。

【請求項２】　前記有機チタン化合物は、ジヒドロキシチタンビスラクテートまたはジヒドロキシチタンビスラクテート誘導体である、請求項１に記載の固体電解質の製造方法。

【請求項３】　前記前駆体溶液は、リン供給源および酸素供給源として、リン酸またはリン酸金属塩を含む、請求項１または２に記載の固体電解質の製造方法。

【請求項４】　リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質であって、

チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液による被膜を基材に対して形成し、当該被膜を加熱して、ゲル化工程を経ずに焼成することによって形成されたことを特徴とする、固体電解質。

【請求項５】　リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質を備えるリチウム電池であって、

前記固体電解質は、チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液による被膜を正極体および／または負極体に対して形成し、当該被膜を加熱して、ゲル化工程を経ずに焼成することによって形成されたことを特徴とする、リチウム電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、リチウムイオン伝導性を有する固体電解質の製造方法、これにより製造される固体電解質、および、リチウム電池に関する。

【０００２】

【従来の技術】リチウム電池は、軽量で高エネルギー密度を有するという特長を備えることから、携帯電話やノートパソコンなどの携帯電子機器におけるメモリ保持電源や駆動電源として用いられることが多い。リチウム電池は、一般に、リチウムイオンを充放電可能な正極活物質を含んでなる正極と、リチウムをドープ・脱ドープ可能な材料やリチウム合金などの負極活物質を含んでなる負極と、正極および負極の間においてリチウムイオンの移動を許容する電解質とを備え、二次電池として構成されている。

【０００３】リチウム二次電池に対しては、近年、携帯情報機器などの小型軽量化に伴い、薄型化および更なる高エネルギー密度化の要求が高まっている。リチウム二次電池の電解質としては、従来、リチウムイオン伝導性の非水系電解液が一般的に用いられていたが、近年では、リチウム二次電池の薄型化および高エネルギー密度化の要求に対応すべく、固体電解質が注目を集めている。

【０００４】固体電解質としては、ゲル電解質、真性ポリマー電解質、および無機固体電解質が知られている。無機固体電解質は、リチウム電池において、高強度であるため薄膜化しても補強材を必要とせず、電極間のセパレータとしても機能することができ、且つ、液漏れを生じることがないため安全性が高い、という利点を有するので、リチウム電池用途の固体電解質として特に注目を集めている。

【０００５】リチウムイオン伝導性を示す無機固体電解質としては、従来より、Li_3N単結晶、ならびに、$LiI-Li_2S-P_2S_5$系、$LiI-Li_2S_2-B_2S_3$系および$LiI-Li_2S-SiS_4$系のガラスが知られている。しかしながら、これらの材料は、化学的・熱的に不安定であるため、リチウム電池の電解質としては実用的でない。

【０００６】そこで、近年、リチウムイオン伝導性を示す無機固体電解質として、ガラスセラミックス系の酸化物固体電解質の研究が活発になっている。代表的なものとしては、一般組成式$LiM(PO_4)_3$（M＝Ｔｉ，Ｚｒ，Ｇｅ，Ｈｆ）で表されるＬＩＳＩＣＯＮ型のものが挙げられる。ＬＩＳＩＣＯＮ型の酸化物固体電解質においては、一般に、Ｍの一部を元素置換することによって、リチウムイオン伝導性の向上が図られる。例えば、上掲の一般組成式においてＭとしてＴｉを選択し、当該Ｔｉの一部がＡｌで置換されている$Li_{1+X}Al_XTi_{2-X}(PO_4)_3$では、室温で$7\times10^{-4}$ Ｓ／ｃｍという高イオン伝導性を達成することが可能である。このようなガラスセラミックス系酸化物固体電解質は、化学的・熱的に比較的安定であり、リチウム電池の固体電解質として有用である。このようなＬＩＳＩＣＯＮ型の酸化物固体電解質を備えるリチウム二次電池は、例えば特開２００２－４２８７６号公報に開示されている。

【０００７】

【発明が解決しようとする課題】酸化物固体電解質などの無機固体電解質の製造においては、従来、溶融法またはゾルーゲル法が採用されている。溶融法は、固相反応により構成元素のネットワークを形成した後、これを冷却して所定の結晶構造を形成する手法である。そのため、原料を固溶体化するために極めて多量の熱を必要とする。また、固相反応の進行は遅いので、反応の完結には長時間を要する。ＬＩＳＩＣＯＮ型固体電解質の製造においては、例えば、まず、粉状の各元素供給源からなる原料混合物を１５００℃程度の高温まで加熱して溶融する。溶融状態を１～２時間維持した後、加熱温度を下げて固溶体ないし固体の状態とし、８００℃程度で１２時間以上加熱する。その後、再び昇温して１０００℃以上で２４時間加熱し、これを冷却して目的とする固体電

解質を得る。このように、溶融法により固体電解質を得るためには、多大な熱および時間を必要とする。加えて、溶融法によると固体電解質は塊状に合成され、当該塊状体からマイクロメートルオーダーの膜厚の固体電解質薄膜を形成するのは困難である。

【０００８】一方、ゾルーゲル法は、溶液系における加水分解反応により構成元素のネットワークを形成した後、これを焼き固めて所定の結晶構造を形成する手法である。そのため、溶融法のような高温工程は必要とされない。しかし、適切なネットワークを形成するためには、穏やかな条件でゆっくりと加水分解を進行させることによって、原料溶液についてゾル状態を経てゲル化しなければならず、溶融法よりも長時間を要する。ＬＩＳＩＣＯＮ型固体電解質の製造においては、例えば、まず、各元素供給源を含むアルコール溶液を２５〜８０℃でゾル化する。次に、当該ゾルを２５〜１２０℃で１日〜１週間程度放置してゲル化させる。その後、８００〜９００℃で１時間程度の加熱焼成を行い、これを冷却して目的とする固体電解質を得る。このように、ゾルーゲル法によると、特にゲル化のために長時間を要する。

【０００９】本発明は、このような事情のもとで考え出されたものであって、リチウムイオン伝導性の固体電解質を低温かつ短時間で製造するための方法、これにより製造される固体電解質、および、そのような固体電解質を備えるリチウム電池を提供することを目的とする。

【００１０】

【課題を解決するための手段】本発明の第１の側面によると、リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質の製造方法が提供される。この製造方法は、チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液を加熱して、ゲル化工程を経ずに焼成することを特徴とする。

【００１１】このような構成の固体電解質の製造方法は、溶液系で構成元素のネットワークを形成した後にこれを焼き固めることによって、リチウムと、チタンと、リンと、酸素とを含んでなる所定の結晶構造を形成する手法であり、ネットワークの形成に際して前駆体溶液の意図的なゲル化工程を経ない。したがって、当該方法によると、長時間を要するゲル化工程を経ずに、例えば、一般組成式$LiM(PO_4)_3$で表されるＬＩＳＩＣＯＮ型固体電解質などを合成することができる。また、溶液系で構成元素のネットワークを形成するという点では本発明に係る方法とゾルーゲル法とは共通し、本発明によっても溶融法のような高温工程を経る必要はない。

【００１２】従来より、固体電解質を合成するためのゾルーゲル法では、アルコール溶液系における加水分解により構成元素ネットワークを形成すべく、チタン供給源として、加水分解され易いチタンアルコキシドが採用されている。チタンアルコキシドは、比較的不安定であり、リン酸（H_3PO_4）またはその金属塩の共存下では、これらの作用により沈殿を生じ易いという性質を有する。固体電解質の合成の過程において、前駆体溶液にて沈殿が生じると、適切な組成の構成元素ネットワークの形成が阻害されてしまい、目的組成の固体電解質を得ることができない。そのため、ゾルーゲル法では、例えばＬＩＳＩＣＯＮ型固体電解質の合成において、リン供給源および酸素供給源としてリン酸（H_3PO_4）またはその金属塩を使用することができず、チタンアルコキシドに作用しない穏やかなリン酸トリエチル、リン酸トリブチル、リン酸アンモニウムがリン・酸素供給源として使用される。これら穏やかなリン酸化合物を使用する場合、構成元素ネットワークにPO_4を適切に取り込むためには、ゆっくりとした加水分解による長時間のゲル化工程を経る必要がある。これは、ネットワークへのPO_4の取り込み過程において、リン酸の酸素原子に結合している嵩高い化学種が充分に解離しつつ当該酸素原子を介してPO_4がネットワークに連結する必要があるためだと考えられる。このように、ＬＩＳＩＣＯＮ型の固体電解質を合成するためのゾルーゲル法では、特にＴｉと共にPO_4を構成元素ネットワークに適切に取り込むために、ゆっくりとした加水分解による長時間のゲル化工程を経る必要があるのである。

【００１３】これに対し、本発明の第１の側面に係る方法は、構成元素ネットワークを形成するためのゲル化工程を経ない。本発明で用いられる前駆体溶液には、チタン供給源として非加水分解性の有機チタン化合物が溶解しており、当該有機チタン化合物は所定の溶液系で比較的安定に存在する。ここで、非加水分解性の有機チタン化合物とは、前駆体溶液にて目的とする構成元素ネットワークが形成されるまでの間、例えばＴｉ−Ｏ−Ｒ結合などのＴｉ近傍の結合に対する酸または塩基による加水分解攻撃を阻害する構造を保持可能な有機チタン化合物をいう。そのような有機チタン化合物としては、例えば、下記の化学式（１）で表されるジヒドロキシチタンビスラクテートやその誘導体が挙げられる。

【００１４】

【化１】

$$\left[(OH)_2Ti-O-\underset{COO^-}{\overset{H}{C}}-CH_3\right]_2\cdot 2H^+ \quad \cdots\cdots\ (1)$$

【００１５】このような非加水分解性の有機チタン化合物が前駆体溶液に溶解している状態では、当該有機チタン化合物のチタン近傍結合は加水分解攻撃から充分に保護されているため、前駆体溶液に添加すべき他元素供給源について、使用可能な化学種の自由度は高い。具体的には、リチウム、リン、酸素などの他元素の供給源としては、チタンに作用して沈殿を生じ易い化学種であっても使用することができるのである。そのため、そのよう

なチタン作用性の化学種の中からでも、ゲル化工程を得ずともネットワーク形成可能な程度に安定な化学種を選択することが可能となる。また、このような安定な他元素供給源を使用することにより、非加水分解性の有機チタン化合物自体も、その安定性に起因して、ゲル化工程を得ずとも適切にネットワークに取り込まれることが可能となる。

【００１６】例えば、ＬＩＳＩＣＯＮ型固体電解質を合成する場合において、チタン供給源である有機チタン化合物としてジヒドロキシチタンビスラクテートを採用すると、リン・酸素供給源として、リン酸（H_3PO_4）またはその金属塩を使用することができる。リン酸またはリン酸金属塩に由来するPO_4^{3-}は、所定の前駆体溶液系において比較的安定に存在し、前駆体溶液がゲル化せずとも、チタンやリチウムなどの他元素とともに適切にネットワークを形成することが可能である。

【００１７】このように、本発明の第１の側面に係る方法によると、前駆体溶液において、チタン供給源として非加水分解性の有機チタン化合物を採用することによって、他元素供給源として、ゲル化工程を経ずともネットワーク形成可能な化学種を使用することができ、その結果、ゲル化工程を経ずに溶液系にて構成元素のネットワークを形成した後にこれを焼き固めることによって、リチウムイオン伝導性の固体電解質を形成することが可能となっている。したがって、本発明の第１の側面に係る方法によると、長時間を要するゲル化工程を経ずに、且つ、溶融法のような高温工程を経ずに、例えばＬＩＳＩＣＯＮ型の固体電解質などを合成することができるのである。

【００１８】本発明の前駆体溶液に含まれるチタン供給源としての有機チタン化合物は、好ましくは、ジヒドロキシチタンビスラクテートまたはジヒドロキシチタンビスラクテート誘導体である。

【００１９】前駆体溶液は、好ましくは、リン供給源および酸素供給源として、リン酸またはリン酸金属塩を含んでいる。前駆体溶液は、好ましくは、リチウム供給源として酢酸リチウムを含んでいる。また、前駆体溶液は、好ましくは、溶媒成分として水を含んでいる。より好ましくは、前駆体溶液は、溶媒成分として水に加えてアルコールを含んでいる。

【００２０】本発明における焼成は、加熱温度５６０℃以上で行う。より好ましくは、焼成の前に、加熱温度５６０℃未満、例えば２５０～４００℃で仮焼成を行う。リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質は、好ましくは、ＬＩＳＩＣＯＮ型固体電解質である。

【００２１】本発明の第２の側面によると、リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質が提供される。この固体電解質は、チタン供給源として非加水分解性の有機チタン化

合物を含む前駆体溶液による被膜を基材に対して形成し、当該被膜を加熱して、ゲル化工程を経ずに焼成することによって形成されたことを特徴とする。

【００２２】本発明の第２の側面に係る固体電解質は、第１の側面に係る方法において用いられるのと同様の前駆体溶液を、スピンコーティングやディップコーティングなどにより所定の基材に対して塗布した後に焼成することによって、形成されるものである。したがって、第２の側面によっても、固体電解質の形成において第１の側面に関して上述したのと同様の効果が奏される。

【００２３】本発明の第３の側面によるとリチウム電池が提供される。このリチウム電池は、リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質を備え、当該固体電解質が、チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液による被膜を正極体および／または負極体に対して形成し、当該被膜を加熱して、ゲル化工程を経ずに焼成することによって形成されたことを特徴とする。

【００２４】本発明の第３の側面に係るリチウム電池は、第１の側面に係る方法において用いられるのと同様の前駆体溶液を、スピンコーティングやディップコーティングなどにより正極体や負極体に対して塗布した後に焼成することによって形成された固体電解質を備えるものである。したがって、第３の側面によっても、固体電解質の形成において第１の側面に関して上述したのと同様の効果が奏される。

【００２５】

【発明の実施の形態】図１は、本発明の第１の実施形態に係る固体電解質の製造方法を表すフローチャートである。本発明に係る固体電解質は、構成元素として少なくともリチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を示す例えばＬＩＳＩＣＯＮ型の固体電解質である。

【００２６】本実施形態の固体電解質の製造においては、まず、前駆体溶液調製工程Ｓ１において前駆体溶液を調製する。前駆体溶液を構成するための溶媒としては、水、または、水とアルコールの混合溶媒を用いる。混合溶媒を構成するためのアルコールとしては、例えばイソプロパノール、エタノールを用いることができる。前駆体溶液調製工程Ｓ１では、これらのような溶媒に対して、合成目的の固体電解質の構成元素を含む原料を添加して溶解させる。このとき、構成元素が所望のモル比で共存するように、前駆体溶液を調製する。また、前駆体溶液には、当該前駆体溶液の粘度を調節するために、増粘剤として、ポリエチレングリコールなどの高分子材料を更に加えてもよい。

【００２７】例えばＬＩＳＩＣＯＮ型固体電解質を製造する際には、リチウム供給源としては、例えば、酢酸リチウム、水酸化リチウム、硝酸リチウム、シュウ酸リチウムを用いることができる。チタン供給源としては、例

えばジヒドロキシチタンビスラクテートやその誘導体を用いることができる。リン供給源としては、例えばリン酸やその金属塩を用いることができる。チタン供給源としてジヒドロキシチタンビスラクテートやその誘導体を用いると、合成完了時に均一な構成元素ネットワークを形成し易い。加えて、ジヒドロキシチタンビスラクテートは、リン供給源であるリン酸やリン酸金属塩由来のPO_4^{3-}との共存安定性が比較的高く、ゲル化工程を経ずに構成元素ネットワークを形成するのに好適である。また、固体電解質のリチウムイオン伝導性を向上すべく、前駆体溶液には、更に、Ｉｎ，Ｓｃ，Ｇａ，Ｃｒ，Ａｌ，またはＦｅなどを硝酸塩、水酸化物、硝酸塩、シュウ酸塩の形態で添加してもよい。このような元素を適切な濃度で前駆体溶液に添加することにより、Ｔｉの一部を置換するように、当該元素をネットワークひいては結晶構造に取り込ませることが可能である。

【００２８】次に、塗布工程Ｓ２において、上述のようにして調製した前駆体溶液を所定の基材上に塗布し、前駆体溶液からなる被膜を基材に対して形成する。塗布手段としては、例えば、スピンコーティング、ディップコーティング、スプレーコーティングを採用することができる。被膜の厚さ、ひいては固体電解質薄膜の厚さは、増粘剤の添加量で調節することが可能である。このような塗布工程を経ることによって、最終的に薄い固体電解質が得られることとなる。固体電解質を薄膜に形成する必要のない場合には、本工程は行わない。

【００２９】次に、加熱焼成工程Ｓ３において、基材上の前駆体溶液被膜または耐熱容器に入れた前駆体溶液を、基材または耐熱容器ごと加熱し、加熱温度５６０～１２００℃で１～５時間焼成する。加熱温度５６０℃以上とすると、前駆体溶液に含まれていた溶媒を蒸散させた後にリン供給源から形成され得る五酸化二リンなどを分解しつつ、焼成することができる。本発明では、このような焼成工程の前に、２５０～４００℃で１～２時間の仮焼成を行ってもよい。このような仮焼成を行うと、各元素供給源に含まれる有機化合物種を本焼成の前に燃焼することができ、その結果、良質の固体電解質を焼結することが可能となる。

【００３０】以上の工程を経た後、適切に冷却することによって、本発明に係るリチウムイオン伝導性の固体電解質が得られる。このように、本発明によると、溶融法より低温かつゾルーゲル法より短時間のプロセスで、リチウムイオン伝導性の固体電解質を得ることができる。このようなリチウムイオン伝導性の固体電解質は、リチウム一次電池やリチウム二次電池の電解質層を構成するための材料として利用することができる。また、本発明では、前駆体溶液は、直接的に焼成工程に付され、焼成前に充分にはゲル化されない。そのため、本発明によると、前駆体溶液により基材上に充分に薄い被膜を形成することができ、その結果、その膜厚に対応する充分に薄いリチウムイオン伝導性固体電解質膜を形成することが可能となる。このような薄いリチウムイオン伝導性固体電解質膜は、リチウム一次電池やリチウム二次電池の電解質層として有用である。

【００３１】図２は、本発明の第２の実施形態に係るリチウム電池Ｘの断面図である。図２に示すように、本発明に係るリチウム電池Ｘは、正極集電層１１および正極層１２からなる正極体１０と、負極集電層２１および負極層２２からなる負極体２０と、正極体１０および負極体２０の間に介在する固体電解質層３０とを備える。本実施形態においては、正極集電層１１および負極集電層２１は、各々、正極缶４１および負極缶４２に対して、集電体４３を介して固定されている。正極缶４１、負極缶４２、および集電体４３は、例えばステンレス鋼製である。正極缶４１と負極缶４２との間は、例えばポリプロピレン製のパッキング材４４で封止されている。集電体４３は、正極集電層１１と正極缶４１の間、および、負極集電層２１と負極缶４２の間の空隙を埋めつつ導通を図るためのものである。このようにして、本実施形態のリチウム電池Ｘは、コイン型リチウム二次電池として構成されている。

【００３２】正極集電層１１および負極集電層２１は、各々、所定の端子すなわち正極缶４１および負極缶４２に対して正極層１２および負極層２２を良好に導通させるためのものであって、高導電性材料により構成される。例えば、アルミニウム、銅、またはニッケルなどを、蒸着、スパッタリング、またはメッキすることによって形成される。或は、ステンレス片を用いて構成してもよい。

【００３３】正極層１２は、粒状の正極活物質と、粒状の導電剤と、樹脂材料よりなる結着剤との混合体として構成されている。

【００３４】正極活物質としては、リチウム－遷移金属複合酸化物を用いることができる。リチウム－遷移金属複合酸化物としては、例えば、リチウムーニッケル複合酸化物（$LiNiO_2$）、リチウムーマンガン複合酸化物（$LiMnO_2$）、リチウムーコバルト複合酸化物（$LiCoO_2$）などが挙げられる。或は、正極活物質としては、リチウムーニッケル複合酸化物（$LiNiO_2$）におけるＮｉの一部が他元素で置換されているリチウムーニッケル系複合酸化物を用いることもできる。

【００３５】正極層１２を形成するための導電剤としては、例えば、アセチレンブラック、グラファイト、カーボンなどが挙げられる。また、正極層１２を形成するための結着剤としては、例えば、ポリエチレンオキシド、エチレンープロピレンージエン三元共重合体などが挙げられる。

【００３６】負極層２２は、粒状の負極活物質と、粒状の導電剤と、樹脂材料よりなる結着剤との混合体として構成されている。

【００３７】負極活物質としては、例えば、チタン酸リチウムやバナジウム酸リチウムなどのリチウム－遷移金属複合酸化物、および、リチウム－アルミニウム合金やリチウム－インジウム合金などのリチウム合金などが挙げられる。また、負極活物質としては、炭素材料を用いてもよい。炭素材料としては、例えば、グラファイト、共役系樹脂（例えば、フェノール樹脂、アクリル樹脂、ポリイミド樹脂、ポリアミド樹脂）、縮合多環炭化水素化合物（例えば、ナフタレン、フェナントレン、アントラセン）、フラン樹脂（例えば、フルフリルアルコール、フリラールのホモポリマー、およびこれらのコポリマー）が挙げられる。これらの炭素材料は、単独でも、複数種を混合して用いてもよく、特にグラファイトが好適に用いられる。

【００３８】負極層２２を形成するための導電剤および結着剤としては、正極層１２に関して上述したのと同様のものを用いることができる。

【００３９】固体電解質層３０は、リチウムイオン導電性を有する無機固体電解質により構成されている。固体電解質層３０は、第１の実施形態に係る固体電解質の製造方法により形成される例えばＬＩＳＩＣＯＮ型の固体電解質である。固体電解質層３０の形成においては、まず、第１の実施形態に関して上述した前駆体溶液を、リチウム電池Ｘの製造プロセスにおいて形成された正極層１２または負極層２２に対してディップコーティングする。次に、加熱処理により、加熱温度５６０～１２００℃で１～５時間焼成する。焼成工程の前には、２５０～４００℃で１～２時間の仮焼成を行ってもよい。このようなディップコーティングから焼成までを所定回数繰り返すことによって、正極層１２上または負極層２２上において、所望の膜厚の固体電解質層３０を形成することができる。本実施形態では、リチウム電池Ｘの他の部位については、公知の手法で形成される。

【００４０】本実施形態のリチウム電池Ｘは、コイン型として構成されているが、本発明に係るリチウム電池については、円筒状、角形、シート型のいずれの形態をも採用することができる。

【００４１】

【実施例】次に、本発明の実施例について記載する。

【００４２】<前駆体溶液の調製>リン供給源としてのリン酸（H_3PO_4、和光純薬工業製）を１０ｗｔ％の濃度で含む水溶液に対して、リチウム供給源としての酢酸リチウム（和光純薬工業製）を、リチウムとリンの存在比が１：３（モル比）となるように添加して混合した。次に、チタン供給源としてのジヒドロキシチタンビスラクテートを含むジヒドロキシチタンビスラクテート溶液（商品名：オルガチックス　ＴＣ－３１０、松本製薬工業製）に対して、上述のようにして調製した水溶液を、リチウムとチタンとリンの存在比が１：２：３（モル比）となるように添加し、これを２３℃で１分間混合することによって、ゾル状の前駆体溶液を調製した。本実施例で用いたジヒドロキシチタンビスラクテート溶液は、ジヒドロキシチタンビスラクテート４３重量部と、水１７重量部と、イソプロパノール４０重量部とからなる。

【００４３】<固体電解質膜の形成>上述のようにして調製した前駆体溶液を、スピンコーティングにより石英ガラス基板（４０ｍｍ×４０ｍｍ）上に塗布した。このとき、石英ガラス基板の回転条件は、１００ｒｐｍで１０秒間、および、これに続いて５００ｒｐｍで１０秒間とした。次に、このようにして前駆体溶液被膜が形成された基板を電気炉に入れ、大気雰囲気下において、８００℃で５時間加熱することによって焼成した。その後、基板を電気炉から取り出して放冷した。このようにして、石英ガラス基板上において薄膜状の固体電解質を形成することができた。

【００４４】このようにして形成された固体電解質薄膜について、ＩＣＰ発光分光分析により化学分析したところ、当該固体電解質を構成するリチウム、チタン、リンのモル比は、前駆体溶液における各元素の存在モル比（１：２：３）に対応していることが判った。また、この固体電解質薄膜について、Ｘ線回折による解析を行ったところ、回折パターンから、結晶相は$LiTi_2(PO_4)_3$で表される化合物であることが判った。更に、この固体電解質薄膜について、接触型膜厚計により膜厚を測定したところ、０．３μｍであった。以上の結果、本実施例によると、ＬＩＳＩＣＯＮ型の固体電解質薄膜を、溶融法よりも低温であって且つ溶融法やゾル－ゲル法よりも短時間で合成できることが判った。また、本実施例によると、前駆体溶液に対して適量の増粘剤を添加すれば、その膜厚をマイクロメートルオーダーで制御可能であることが判った。

【００４５】以上のまとめとして、本発明の構成およびそのバリエーションについて、以下に付記として列挙する。

【００４６】（付記１）リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質の製造方法であって、チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液を、ゲル化工程を経ずに焼成することを特徴とする、固体電解質の製造方法。

（付記２）前記有機チタン化合物は、ジヒドロキシチタンビスラクテートまたはジヒドロキシチタンビスラクテート誘導体である、付記１に記載の固体電解質の製造方法。

（付記３）前記前駆体溶液は、リン供給源および酸素供給源として、リン酸またはリン酸金属塩を含む、付記１または２に記載の固体電解質の製造方法。

（付記４）前記前駆体溶液は、リチウム供給源として酢酸リチウムを含む、付記１から３のいずれか１つに記載

の固体電解質の製造方法。

（付記５）前記前駆体溶液は、溶媒成分として水を含む、付記１から４のいずれか１つに記載の固体電解質の製造方法。

（付記６）前記前駆体溶液は、溶媒成分としてアルコールを含む、付記５に記載の固体電解質の製造方法。

（付記７）前記焼成における加熱温度は、５６０℃以上である、付記１から６のいずれか１つに記載の固体電解質の製造方法。

（付記８）前記焼成の前に加熱温度２５０～４００℃で仮焼成を行う、付記７に記載の固体電解質の製造方法。

（付記９）前記固体電解質は、ＬＩＳＩＣＯＮ型固体電解質である、付記１から８のいずれか１つに記載の固体電解質の製造方法。

（付記１０）リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質であって、チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液による被膜を基材に対して形成し、当該被膜を加熱して、ゲル化工程を経ずに焼成することによって形成されたことを特徴とする、固体電解質。

（付記１１）リチウムと、チタンと、リンと、酸素とを含んでリチウムイオン伝導性を有する固体電解質を備えるリチウム電池であって、前記固体電解質は、チタン供給源として非加水分解性の有機チタン化合物を含む前駆体溶液による被膜を正極体および／または負極体に対して形成し、当該被膜を加熱して、ゲル化工程を経ずに焼＊＊成することによって形成されたことを特徴とする、リチウム電池。

【００４７】

【発明の効果】本発明によると、リチウムイオン伝導性の固体電解質を、溶融法よりも低温であって、且つ、溶融法やゾルーゲル法よりも短時間で合成することができる。更に、本発明によると、リチウムイオン伝導性固体電解質をマイクロメートルオーダーで薄膜形成可能である。

【図面の簡単な説明】

【図１】本発明に係る固体電解質の製造方法についてのフローチャートである。

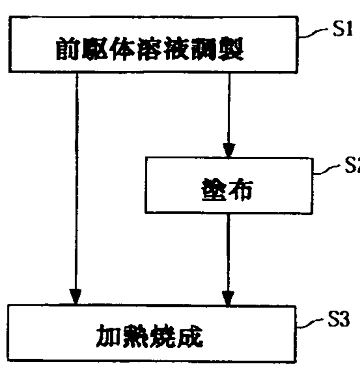
【図２】コイン型として形成された本発明に係るリチウム電池の断面図である。

【符号の説明】

Ｓ１	前駆体溶液調製工程
Ｓ２	塗布工程
Ｓ３	加熱焼成工程
１０	正極体
１１	正極集電層
１２	正極層
２０	負極体
２１	負極集電層
２２	負極層
３０	固体電解質層

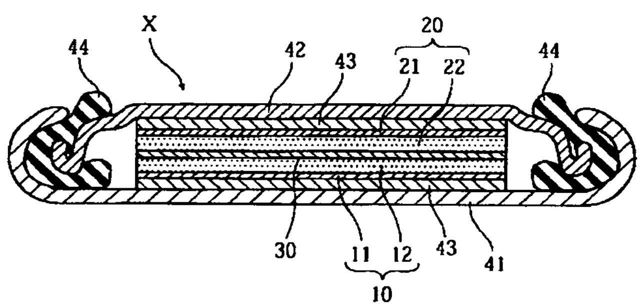
【図１】

本発明の固体電解質製造方法のフローチャート



【図２】

本発明のリチウム電池



フロントページの続き

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